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Comparison of VFA titration procedures used for monitoring the biogas process

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ABSTRACT

Titrimetric determination of volatile fatty acids (VFAs) contents is a common way to monitor a biogas process. However, digested manure from co-digestion biogas plants has a complex matrix with high concentrations of interfering components, resulting in varying results when using different titration procedures. Currently, no standardized procedure is used and it is therefore difficult to compare the performance among plants. The aim of this study was to evaluate four titration procedures (for determination of VFA-levels of digested manure samples) and compare results with gas chromatographic (GC) analysis. Two of the procedures are commonly used in biogas plants and two are discussed in literature. The results showed that the optimal titration results were obtained when 40 mL of four times diluted digested manure was gently stirred (200 rpm). Results from samples with different VFA concentrations (1–11 g/L) showed linear correlation between titration results and GC measurements. However, determination of VFA by titration generally overestimated the VFA contents compared with GC measurements when samples had low VFA concentrations, i.e. around 1 g/L. The accuracy of titration increased when samples had high VFA concentrations, i.e. around 5 g/L. It was further found that the studied ionisable interfering components had lowest effect on titration when the sample had high VFA concentration. In contrast, bicarbonate, phosphate and lactate had significant effect on titration accuracy at low VFA concentration. An extended 5-point titration procedure with pH correction was best to handle interferences from bicarbonate, phosphate and lactate at low VFA concentrations. Contrary, the simplest titration procedure with only two pH end-points showed the highest accuracy among all titration procedures at high VFA concentrations. All in all, if the composition of the digested manure sample is not known, the procedure with only two pH end-points should be the procedure of choice, due to its simplicity and accuracy.

1. Introduction

Monitoring and control of the biogas process is important in order to keep optimal operating conditions and avoid process failure incidents. Many parameters have been used for monitoring the biogas process, such as pH, volatile fatty acid (VFA) concentrations, bicarbonate alkalinity/buffer capacity, gas production and gas composition. The concentration of VFAs is one of the most common parameters used to monitor

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the biogas process. Several studies from full-scale biogas plants showed that the contents of VFAs are a good parameter for monitoring the biogas process (Ahring et al., 1995). It gives a good indication of the activity and state of the anaerobic microorganisms in the biogas reactors. Individual VFAs are commonly measured by gas chromatography (GC) with flame ionization detection (FID), otherwise total VFAs can be determined by titration of the samples, which is cheaper and widely used in commercially operated biogas plants (Anderson and Yang, 1992).

Digested manure contains several compounds, such as ammonia, sulphide, phosphate and high concentration of bicarbonate which can interfere with the VFA titration. Presently, most of the full-scale biogas plants in Denmark use the titration technique for measurement of VFA for process monitoring. In this study, four titration procedures were tested. Two of the procedures are commonly used in Danish biogas plants for VFA determination, namely the simple titration procedure by Anderson and Yang (1992) and a modified version of the 2-step back titration by Ellegaard (1990). The other two procedures from literature are the 4-point titration proposed by Buchauer (1988) based on the theory from Kapp (1984) and known from its use in high rate anaerobic digesters (De Prijkels et al., 2004) and the 5-point titration approach by Moosbrugger et al. (1993a, 1993c), known from applications in wastewater treatment plants. The latter has been applied with high accuracy in many anaerobic samples, e.g. raw wastewater, primary sludge, digested sludge and winery waste (e.g. Moosbrugger et al., 1993b). However, they have never been tested with digested manure. Since these procedures apply direct titration which is easy to implement in the laboratory, the procedure of VFA monitoring can be even more user friendly.

The four procedures mentioned above were used to determine the total VFA concentration in digested manure samples with different VFA and alkalinity concentrations. The VFA results from titration were compared with the VFA measurement by gas chromatography (GC) as the common reference method. Since the biogas plants work as co-digestion plants, treating manure together with different organic wastes where ammonia, phosphate, sulphide and lactate could be present in significant amounts in the digester, the influence of these components on VFA measurements by titration was also investigated. The comprehensive investigation of the effect of these parameters in digested manure based on different titration procedures has never been conducted and needs to be clarified in order to interpret the titration results correctly and to be able to compare the data among biogas plants.

2. Theory

Determination of VFAs by titration is based on the equilibrium of VFAs in their dissociated and non-dissociated forms. The concentration of VFAs is calculated from the amount of acid/base consumed to change the VFAs between these forms. During titration, other chemical components in the sample will also consume acid/base, such as bicarbonate, phosphate, ammonium and sulphide, where bicarbonate contributes to the main part of the sample alkalinity. When pH changes the distribution of each species will also change according to the Henderson–Hasselbalch equation. Table 1 shows the pK_a-values of different components typically found in digested manure.

As seen in Table 1, the pK_a-values are quite similar for all the most common VFAs, i.e. around 4.8. This makes determination of individual VFAs by titration difficult and no application of this has been reported. As also seen from Table 1, the other components have pK_a-values that are only slightly different from the target VFAs' pK_a-values. This means, that only a very precise titration may enable determination of the VFA level, without influence from the interfering components, as will be studied in this work.

2.1. The simple titration procedure

The simple titration procedure proposed by Anderson and Yang (1992) applies the direct titration of the sample from the initial pH to two pH end-points (5.1 and 3.5). This is the simplest titration procedure compared in this study. The calculation of the VFA concentration is based on the assumption that the acid titration volume correlates with the change in equilibration of the VFA and carbonate alkalinity subsystems as seen in the following equations:

$$A1 = \frac{[HCO_3^-]\cdot([H]_2 - [H]_1)}{([H]_2 + K_1)} + \frac{[VFA]\cdot([H]_2 - [H]_1)}{([H]_2 + K_2)} \quad (1)$$

$$A2 = \frac{[HCO_3^-]\cdot([H]_3 - [H]_1)}{([H]_3 + K_1)} + \frac{[VFA]\cdot([H]_3 - [H]_1)}{([H]_3 + K_2)} \quad (2)$$

where

- -A1 and A2 are the molar equivalents of acid consumed to the first and second pH end-point
- -$[HCO_3^-]$ is the bicarbonate concentration
- -[VFA] is the VFA ion concentration
- -$[H]_{1,2,3}$ are the hydrogen ion concentrations of the original sample, at the first and the second pH end-point
- K_1 is a conditional disassociation constant of carbonic acid, $3.2\cdot10^{-7}$, and
- K_2 is a combined dissociation constant of the VFA (C_2 to C_5), $2.4\cdot10^{-5}$

The two equations are solved to give both the bicarbonate and the total VFA concentration, see details on the calculation principle in Anderson and Yang (1992).

2.2. The 2-step back titration procedure

The second procedure is the modified 2-step back titration where the CO_2 is removed by aerating the sample (Ellegaard, 1990), in comparison to the original, which used boiling (Dilallo and Albertson, 1961). The removal of biocarbonate was shown to eliminate the interference from bicarbonate on VFA titration, and thus obtain more accurate VFA results. The sample was first acidified by 1.0 M HCl to pH 3 to change all bicarbonates to the form of $H_2CO_3 \leftrightarrow CO_2$ and aerating the sample to remove CO_2. The sample was then back titrated